

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-043892
 (43)Date of publication of application : 16.02.2001

(51)Int.Cl. H01M 10/36
 H01M 6/18

(21)Application number : 11-214846

(71)Applicant : KYOCERA CORP

(22)Date of filing : 29.07.1999

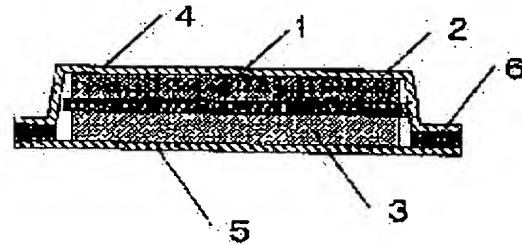
(72)Inventor : MISHIMA HIROMITSU
 UMAGOME SHINJI
 KAMIMURA TOSHIHIKO
 KITAHARA NOBUYUKI
 HARA TORU
 OSAKI MAKOTO
 HIGUCHI HISASHI

(54) LITHIUM BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a lithium battery cleared of a problem carried by a conventional lithium battery that safety is impaired by the low heat resistance of battery component materials.

SOLUTION: This lithium battery is made by interposing an electrolyte layer 2 between a positive-electrode layer 1 and a negative-electrode layer 3 and sealing them in a battery jar comprising a positive-electrode battery jar 4 and a negative-electrode battery jar 5. The positive-electrode layer 1 and the negative-electrode layer 3 are each formed of an active material and an inorganic solid electrolyte, the electrolyte layer 2 is formed of an inorganic solid electrolyte, the positive-electrode battery jar 4 and the negative-electrode battery jar 5 are each formed of a sheet made of metal, and peripheral parts of the positive-electrode battery jar 4 and of the negative-electrode battery jar 5 are airtightly sealed with insulating ceramics provided with a metallized part on its surface.



LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision
of rejection]

[Date of requesting appeal against examiner's
decision of rejection]

[Date of extinction of right]

*** NOTICES ***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] In the lithium cell enclosed in the battery case which an electrolyte layer is made to intervene between a positive-electrode layer and a negative-electrode layer, and consists of a positive-electrode battery case and a negative-electrode battery case While forming said positive-electrode layer and negative-electrode layer with an active material and an inorganic solid electrolyte, forming said electrolyte layer with an inorganic solid electrolyte and forming said positive-electrode battery case and negative-electrode battery case with metal sheet metal The lithium cell characterized by carrying out the hermetic seal of the periphery section of this positive-electrode battery case and a negative-electrode battery case through the insulating ceramics which prepared the metalization section in the front face.

[Claim 2] The lithium cell according to claim 1 characterized by said positive active material and a negative-electrode active material being transition-metals oxide.

[Claim 3] The lithium cell according to claim 1 or 2 characterized by said metal sheet metal consisting of either stainless steel, aluminum, nickel, copper, covar, 42 alloys, titanium or an aluminium alloy.

[Claim 4] Claim 1 characterized by forming the confrontation section with said electrode layer of said positive-electrode battery case and/or a negative-electrode battery case in a concave thru/or a lithium cell according to claim 3.

[Translation done.]

*** NOTICES ***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention] Especially this invention relates to the lithium cell with which an electrode layer and an electrolyte layer consist of an inorganic substance about a lithium cell.

[0002]

[Description of the Prior Art] The need of the cell as the power source is also increasing quickly with remarkable development of the recent years of the pocket device represented by a cellular phone and the personal computer. Since an atomic weight is a cell using a small lithium with big ionization energy, especially a lithium cell is briskly studied as a cell which can obtain a high energy consistency, and has come to be used for large areas including the power source of a pocket device now.

[0003] Although it roughly divides into these lithium cells and there are cylindrical and a square shape in them, it has structure which the positive electrode and the negative electrode inserted the electrode group wound through the separator into the battery case can, poured all in there, and obturated the organic electrolytic solution.

[0004] Generally in the lithium cell, the cobalt acid lithium (LiCoO_2) and the manganic acid lithium (LiMn_2O_4) are used as positive active material. Carbon materials, such as corks and a carbon fiber, are used for the negative-electrode active material. This LiCoO_2 and LiMn_2O_4 Charge and discharge voltage is about 4V. On the other hand, the charge and discharge voltage of a carbon material is the 0V neighborhood. Therefore, the lithium cell has attained the high voltage beyond nominal-voltage 3.5V by combining these positive active material and negative-electrode active materials.

[0005] However, since these lithium cells are using the inflammable high low-boiling point organic solvent for an electrolyte, its operating temperature range is narrow and they have the problem that it cannot be used, at the elevated temperature exceeding especially 60 degrees C.

Furthermore, if rapid generation of heat takes place at the time of abnormalities, such as overcharge and a short circuit, it is inherent in the danger of resulting in emitting smoke, a burst, or ignition.

[0006] Then, in order to solve the problem on these insurance, development of all the solid-state lithium cells excellent in the thermal resistance using the inorganic solid electrolyte which consists of noncombustible inorganic solid materials, and dependability is furthered. As an example of the lithium cell which used the inorganic solid electrolyte for the electrolyte, there is a thing using sulfide glass as a solid electrolyte so that it may be indicated by JP,11-7942,A, for example.

[0007] However, all the solid-state lithium cells indicated by JP,11-7942,A use for sheathing the cell case of a coin mold or a carbon button mold by which caulking obturation is carried out through the gasket made of resin in the conventional obturation section, and these can never say that thermal resistance is high, and cannot secure the large operational temperature range and large safety which are the features of the cell using a solid electrolyte.

[0008] Moreover, although pasting up and obturating a metal battery case through thermal melting arrival nature resin is proposed by the film cell or the card cell so that it may be

indicated by JP,7-6743,A and JP,8-83596,A, for example, now, thermal resistance will fall more than a gasket.

[0009] This invention is made in view of the trouble of the above conventional lithium cells, and since the thermal resistance of a cell component is low, it aims at offering the lithium cell which canceled the trouble of the conventional lithium cell that safety is low.

[0010]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, the lithium cell of this invention In the lithium cell enclosed in the battery case which an electrolyte layer is made to intervene between a positive-electrode layer and a negative-electrode layer, and consists of a positive-electrode battery case and a negative-electrode battery case While forming said positive-electrode layer and negative-electrode layer with an active material and an inorganic solid electrolyte, forming said electrolyte layer with an inorganic solid electrolyte and forming said positive-electrode battery case and negative-electrode battery case with metal sheet metal The hermetic seal of the periphery section of this positive-electrode battery case and a negative-electrode battery case was carried out through the insulating ceramics which prepared the metalization section in the front face.

[0011] It is desirable for said positive active material and a negative-electrode active material to consist of a transition-metals oxide in the above-mentioned lithium cell.

[0012] Moreover, it is desirable for said metal sheet metal to consist in the above-mentioned lithium cell of either stainless steel, aluminum, nickel, copper, covar, 42 alloys, titanium or an aluminium alloy.

[0013] Moreover, it is desirable to form the confrontation section with the electrode layer of said positive-electrode battery case and/or a negative-electrode battery case in a concave in the above-mentioned lithium cell.

[0014]

[Function] As mentioned above, if a battery case is formed with metal sheet metal and a hermetic seal is carried out through the insulating ceramics, all components will have thermal resistance and incombustibility, and will not result in emitting smoke, a burst, or ignition by rapid generation of heat, either, and safety will be secured.

[0015] Moreover, if positive active material and a negative-electrode active material are used as transition-metals oxide, also when a cell overcharges, a deposit of a metal lithium will not take place, but the dependability of a cell will improve.

[0016] Furthermore, when stainless steel, aluminum, nickel, copper, covar, 42 alloys, titanium, or an aluminium alloy is used for the metallic thin plate made into a battery case, the metal plate of an electrode group stowage was fabricated to the concave in addition and it is heated by welding at the time of the closure, the residual stress which a battery case does not cause too much deformation and is applied to the closure section can be eased, and the dependability of the closure section can be raised.

[0017]

[Embodiment of the Invention] Hereafter, the operation gestalt of the lithium cell of this invention is explained. Drawing 1 is the sectional view showing the example of a configuration of the lithium cell concerning this invention. For an electrolyte layer and 3, as for a positive-electrode battery case and 5, in drawing 1, a negative-electrode layer and 4 are [1 / a positive-electrode layer and 2 / a negative-electrode battery case and 6] the closure sections. Drawing 2 is the expanded sectional view of the closure section of the lithium cell concerning this invention. For the insulating ceramics and 8, as for a nickel-plating layer and 10, in drawing 2, the metalization section and 9 are [7 / a silver solder layer and 11] seal frames.

[0018] The positive-electrode layer 1 and the negative-electrode layer 3 mainly consist of an active material and an inorganic solid electrolyte. The following transition-metals oxides are mentioned as an active material used for the positive-electrode layer 1 and the negative-electrode layer 3. For example, a lithium manganese multiple oxide, a manganese dioxide, lithium nickel complex oxide, a lithium cobalt multiple oxide, a lithium nickel cobalt multiple oxide, a lithium vanadium multiple oxide, a lithium titanium multiple oxide, titanium oxide, niobium oxide, a vanadium oxide, tungstic oxide, etc. and those derivatives are mentioned. Here, what shows more

**** potential to a positive electrode for what a clear distinction does not have in positive active material and a negative-electrode active material, compares the charge and discharge potential of two kinds of transition-metals oxides, and shows electropositive potential more can be used for a negative electrode, respectively, and the cell of the electrical potential difference of arbitration can be constituted. If transition-metals oxide is used for positive active material and a negative-electrode active material, also when a cell overcharges, a deposit of a metal lithium will not take place, but the dependability of a cell will improve.

[0019] To the inorganic solid electrolyte used for the positive-electrode layer 1, the negative-electrode layer 3, and the electrolyte layer 2 Li1.3 aluminum0.3 Ti1.7 3 [for example,] (PO₄)₃Li_{3.6} germanium 0.6V0.4O₄ etc. -- a crystalline substance solid electrolyte -- 30Li₁-41Li₂O-29P₂O₅ 40Li(s)2 O-35 B-2 O₃-25LiNbO₃, Oxide system noncrystalline solid electrolytes, such as 10Li₂O-25 B-2 O₃-15SiO₂-50ZnO, 45Li₁-37Li₂S-18P₂S₅ Li₃PO₄-63Li₂S-36SiS₂ etc. -- a sulfide system noncrystalline solid electrolyte etc. can be mentioned.

[0020] The positive-electrode layer 1 consists of the porous body or precise object which added and carried out pressing of the shaping assistant to positive active material and an inorganic solid electrolyte, and heat-treated it to them, and the negative-electrode layer 3 consists of the porous body or precise object which used as the active material the transition-metals oxide which has **** charge and discharge potential rather than the charge and discharge potential of the positive active material in the positive-electrode layer 1.

[0021] In order to produce the positive-electrode layer 1 and the negative-electrode layer 3, make the water or the solvent in which the shaping assistant was dissolved distribute (1) active material and an inorganic solid electrolyte, and a slurry is prepared. How to heat-treat what carried out pressing and was judged after applying this slurry on the base material film and drying. Or add and corn a direct or shaping assistant and the mixture of (2) active materials and an inorganic solid electrolyte is fed into metal mold. After carrying out pressing of the approach of heat-treating after carrying out pressing with a press machine, and the mixture which carried out (3) granulation with a roll press machine and processing it in the shape of a sheet, the approach of cutting out and heat-treating the sheet etc. is used. Even if the granulation of (2) and (3) is dry type granulation which does not use a solvent even if it is the wet agglomeration which corns from the slurry stated by the approach of (1), it is not cared about.

[0022] The electrolyte layer 2 is producible by producing and heat-treating a Plastic solid only from an inorganic solid electrolyte and a shaping assistant like above-mentioned process (1) - (3).

[0023] As an approach of producing the electrode group which comes to carry out the laminating of the positive-electrode layer 1, the above-mentioned negative-electrode layer 3, and the above-mentioned electrolyte layer 2 How to carry out the specified quantity laminating of each class which heat-treated according to the individual and was used as the porous body or the precise object, and heat-treat it through the electrolyte layer 2 before heat-treating the approach of carrying out a specified quantity laminating, and the positive-electrode layer 1 and the negative-electrode layer 3 after heat treatment, the approach of carrying out the specified quantity laminating of each class before heat treatment, bundling it up, and heat-treating it, etc. can be considered.

[0024] Anyway, as an usable shaping assistant, one sort or two sorts or more of mixture, such as polytetrafluoroethylene, polyacrylic acid, a carboxymethyl cellulose, polyvinylidene fluoride, polyvinyl alcohol, diacetyl cellulose, hydroxypropylcellulose, the poly butyral, polyvinyl chloride, and a polyvinyl pyrrolidone, is mentioned here, for example.

[0025] As a base material film, metallic foils, such as resin films, such as polyethylene terephthalate, polypropylene, polyethylene, and polytetrafluoroethylene, aluminum, stainless steel, and copper, etc. are usable, for example.

[0026] The metal sheet metal used for the positive-electrode battery case 4 and the negative-electrode battery case 5 is limited to neither the manufacture approach nor especially purity that what is necessary is just stainless steel, aluminum, nickel, copper, covar, 42 alloys, titanium, or an aluminium alloy. Moreover, the adjustment of a coefficient of thermal expansion can be taken, and it is satisfactory even if the classes of metallic thin plate used for a positive-

electrode battery case and a negative-electrode battery case differ through the insulating ceramics 7, if a hermetic seal is possible. Suitable thickness should be chosen from the field of the reinforcement as the existence and the sheathing material of a pinhole although it is desirable to use a thin thing from a viewpoint of the energy density of a cell as for board thickness. For example, in the case of covar, it is desirable to be referred to as 30 micrometers or more. It is desirable to be referred to as 500 micrometers or less on the other hand in the thicker one from a viewpoint of constraint by the closure approach, the bonding strength of the closure section, or energy density.

[0027] The confrontation section with the electrode layer of the positive-electrode battery case 4 may be fabricated to a concave, and the existing conventional technique can be used for this concave shaping approach. For example, press working of sheet metal by shaping metal mold is common. That a configuration is seen from an electrode group stowage and should just be a concave, although neither the depth nor especially a dimension is limited, it should make the dimension and the configuration where an electrode group and a battery case 4 can contact in consideration of the thickness of an electrode group, and the thickness of the insulating ceramics 7 in a field. Moreover, in case it fabricates depending on the shaping approach, a concave electrode group stowage serves as a trapezoid, or it is satisfactory in any way by considering as the design of the arbitration which it may be more convenient to establish a curved surface in a flection, and was suitable for the shaping approach.

[0028] As insulating ceramics 7 concerning this invention, although an alumina, a steatite, a mullite, zircon, a glass ceramic, aluminum nitride, etc. can be used, if a price, an electrical property, a mechanical property, etc. are taken into consideration, the alumina of 90% or more of purity which uses an aluminum oxide (aluminum 2O3) as a principal component is suitable.

[0029] In order to produce the insulating ceramics 7 which formed the metalization section 8 in the front face, an annular alumina sintered compact can be first produced from an alumina raw material, then metallizing of Mo and Mn can be carried out, nickel plating can be performed to the front face, and the approach of carrying out silver soldering of the metal which can be welded to battery cases 4 and 5 can be used.

[0030] In order to produce the annular alumina sintered compact 7 from an alumina raw material (1) Make the water or the solvent in which the shaping assistant was dissolved distribute alumina raw material powder, and a slurry is prepared. How to sinter what was judged annularly, after applying this slurry on a base material film and drying, Or add and corn a direct or shaping assistant and (2) alumina raw materials are fed into metal mold. After carrying out pressing of the approach of sintering after carrying out pressing with a press machine, and the mixture which carried out (3) granulation with a roll press machine and processing it in the shape of a sheet, the approach of cutting out the sheet annularly and sintering it etc. is used. Even if the granulation of (2) and (3) is dry type granulation which does not use a solvent even if it is the wet agglomeration which corns from the slurry stated by the approach of (1), it is not cared about.

[0031] Next, the approach of often mixing both, adding a binder using the impalpable powder of Mo and Mn for metalizing both sides of the above-mentioned alumina sintered compact 7, considering as the shape of a paste, applying to the alumina sintered compact front face which performed surface polish and surface treatment beforehand, carrying out elevated temperature baking all over the hydrogen furnace of a humidification ambient atmosphere, and making a metallized layer (metalization section) 8 forming can be use.

[0032] Electrolysis plating and an electroless deposition method can be used for formation of the nickel-plating layer 9. In addition, it is desirable to perform sintering, in order to raise adhesion with the metallized layer 8 of a substrate, while carrying out eburnation of the nickel-plating layer 9.

[0033] Junction in the seal frame 11 and the nickel-plating layer 9 which consist of a metal is possible at the thing which will shine through the silver solder layer 10 and which is attached and done. However, since suitable wax material is selected by the class of metal used for a seal frame, the silver solder layer 10 is not necessarily silver solder.

[0034] In the approach of producing the insulating ceramics 7 which formed the metalization

section 8 in the front face. The conductive paste of refractory metals, such as Mo and W, is screen-stenciled to the alumina Plastic solid which is not calcinated other than the above-mentioned metallizing method. Calcinate, after printing thickly the coincidence calcinating method calcinated collectively and the conductive paste which consists of a metal powder, low melting glass, and an organic binder by screen-stencil on an alumina sintered compact, and the organic substance is removed. There is physical vapor deposition in which a metal layer is made to form with physical vapor deposition which makes a metal fix with low melting glass, such as a thick-film method, vacuum deposition, and sputtering.

[0035] CO₂ of existing [welding / with a seal frame 11 and a battery case] I will use the alloy of the micro parallel seam conjugation method which is a kind of laser-welding methods, such as gas laser and an YAG laser, and a resistance welding method, and a Pb-Sn system and an Au-Sn system, and law can be applied.

[0036] That what is necessary is just the structure contained by the metal sheet metal battery case to which the closure of the electrode group to which the laminating of the positive-electrode layer 1, the electrolyte layer 2, and the negative-electrode layer 3 which consist of an inorganic solid material was carried out was carried out through the insulating ceramics 7, even if the lithium cell of this invention is a primary cell and it is a rechargeable battery, it does not interfere. Moreover, an electrolyte should just be an inorganic solid material which has ion conductivity, and also any, such as rectangular heads, such as a card mold, a film mold, and a flat mold, a trigonum, and a round shape, are sufficient as a cell configuration.

[0037]

[Example] Hereafter, this invention is explained in more detail based on an example.

[0038] The [example 1] lithium hydroxide and the manganese dioxide were mixed so that the mole ratio of Li and Mn might be set to 1:2, by carrying out heating baking of this mixture at 700 degrees C among atmospheric air for 15 hours, the lithium manganese multiple oxide (LiMn₂O₄) was prepared, and this was made into positive active material. Next, the lithium hydroxide and the titanium dioxide were mixed so that the mole ratio of Li and Ti might be set to 4:5, and by carrying out heating baking of this mixture at 750 degrees C in atmospheric air for 15 hours, the lithium titanium multiple oxide (Li₄Ti₅O₁₂) was prepared, and it considered as the negative-electrode active material.

[0039] This LiMn₂O₄ 10Li₂O-25B-2O₃-15SiO₂-50ZnO was blended dryly by the weight ratio 80:20, and it considered as mixed powder each of Li₄Ti₅O₁₂, an inorganic solid electrolyte, and here. In addition, toluene was added further and the slurry was prepared so that the polyvinyl butyral of a shaping assistant might be set to 10 by the weight ratio to this mixed powder 100. Pressurization compression molding of what was made to dry after applying this slurry on a polyethylene terephthalate (PET) film, and was fabricated in the shape of a sheet was carried out by the roll press, the positive electrode was used into the thickness of 0.5mm, and the negative electrode was used as the sheet with a thickness of 0.5mm. Each sheet was pierced with metal mold and sheet-like the positive electrode and negative-electrode Plastic solid of 20mm angle were acquired.

[0040] Next, the polyvinyl butyral of a shaping assistant was mixed with the inorganic solid electrolyte by the weight ratio 100:10, toluene was added further, the slurry was prepared, and the Plastic solid of 20mm angle and the shape of a sheet with a thickness of 0.2mm was produced by fabricating the same on a PET film and judging.

[0041] The laminating of the above-mentioned positive-electrode layer 1 and the negative-electrode layer 3 was carried out through the electrolyte layer 2, package heat treatment of this was carried out at 550 degrees C among atmospheric air, and 18mm angle and the electrolyte layer 2 with a thickness of 0.85mm were produced. The metallic thin plate which judged the covar material with a same thickness of 0.1mm which performed nickel plating on 25mm square was used for the positive-electrode battery case 4 and the negative-electrode battery case 5. However, what fabricated the electrode group stowage by press forming to the concave beforehand was used for the positive-electrode battery case. Width of face of 5mm which carried out silver soldering of the seal frame 10 made from covar by the metallizing method beforehand, and the thing which welded the annular insulating ceramics 7 with a thickness of

0.3mm with the parallel seam conjugation method were used for the negative-electrode battery case 5.

[0042] After having arranged the electrode group in the center of the negative-electrode battery case 5, the card mold lithium cell which put the positive-electrode battery case 4, closed the periphery section of the positive-electrode battery case 4 with the micro parallel seam conjugation method, and was shown in drawing 1 was produced.

[0043] The card mold lithium cell was assembled like the example 1 except having produced the [example 2] positive-electrode battery case 4, the negative-electrode battery case 5, and the seal frame 11 by stainless steel 304.

[0044] It contained to the space surrounded by the polyolefin resin which has an adhesive property to the covar which is a battery case about the electrode group produced like the [example 1 of comparison] example 1, and this covar, and which was fabricated annularly, and it heated, pressurizing with a 140-degree C hot platen, the battery case was sealed, and the card mold lithium cell was produced.

[0045] The card mold lithium cell was assembled like the example 1 except having used for the [example 2 of comparison] positive-electrode battery case the metallic thin plate made from covar which has not processed the electrode group stowage into a concave.

[0046] The purpose which evaluates thermal resistance using the cell produced in the above-mentioned examples 1 and 2 and the examples 1 and 2 of a comparison estimated capacity degradation by elevated-temperature neglect. After evaluation checked that left it in the 100 or 125,150,175,200-degree C thermostat for 100 hours, took out out of the tub, and the temperature of a cell had become a room temperature after preparing each five cells and carrying out a full charge to 2.9V with the current value of the rate of 10 time amount at a room temperature first, it was performed by the approach of carrying out constant-current discharge to 1.5V with the current value of the same rate of 10 time amount as charge, calculating discharge capacity, and searching for the charge-and-discharge effectiveness over a previous charge capacity. The result is as being shown in Table 1.

[0047]

[Table 1]

	充放電効率 (%)				
	100℃	125℃	150℃	175℃	200℃
実施例 1	9.8	9.8	9.8	9.8	9.8
実施例 2	9.8	9.8	9.8	9.8	9.8
比較例 1	9.8	9.2	3.1	1.4	0
比較例 2	9.8	7.1	1.6	0	0

$$\text{充放電効率} (\%) = (\text{放電容量} / \text{充電容量}) \times 100$$

[0048] The decline in the charge-and-discharge effectiveness by elevated-temperature neglect is not seen at all, but its effectiveness of this invention is remarkable in the range to 200 degrees C evaluated by the example to the example of a comparison so that clearly from Table 1. Since the cause that charge-and-discharge effectiveness fell in the range of 150 degrees C or more in the example 1 of a comparison has the low thermal resistance of resin, it is presume to be what resin fused, and moisture invaded in the cell from the sealing section, reacted with the lithium in an active material, and caused irreversible capacity degradation during elevated-temperature neglect. Moreover, since the residual stress at the time of sealing could not be borne, but the crack arose and moisture invaded in the cell when the sealing section was heated, since the electrode group stowage of a battery case was not fabricated to a concave, the capacity fall of the example 2 of a comparison is considered. However, the thickness of an electrode group is thin, or since the residual stress produced in the sealing section becomes small when the thickness of the metallic thin plate of a battery case is thin, it is thought that a crack is not generated.

[0049] Therefore, invasion of moisture is prevented by welding the battery case which consists of the product made from a metallic thin plate which does not have a pinhole through the insulating ceramics, and the large operational temperature range of all solid-state lithium cell original and high safety can be realized. In addition, although an example did not indicate the example of active materials other than metal [other than covar and stainless steel] and LiMn₂O₄, and Li₄Ti₅O₁₂, all are the existing ingredients and it is clear that the same effectiveness is acquired.

[0050]

[Effect of the Invention] as mentioned above, in the lithium cell concerning this invention While forming a positive-electrode layer and a negative-electrode layer with an active material and an inorganic solid electrolyte, forming an electrolyte layer with an inorganic solid electrolyte and forming a positive-electrode battery case and a negative-electrode battery case with metal sheet metal Since the periphery section of this positive-electrode battery case and a negative-electrode battery case was closed through the insulating ceramics which prepared the metalization section in the front face, the thermal resistance of the closure section of a battery case improves, and the large operational temperature range of all solid-state lithium cell original and high safety can be realized.

[Translation done.]

*** NOTICES ***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

TECHNICAL FIELD

[Field of the Invention] Especially this invention relates to the lithium cell with which an electrode layer and an electrolyte layer consist of an inorganic substance about a lithium cell.

[Translation done.]

*** NOTICES ***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

EFFECT OF THE INVENTION

[Effect of the Invention] as mentioned above, in the lithium cell concerning this invention While forming a positive-electrode layer and a negative-electrode layer with an active material and an inorganic solid electrolyte, forming an electrolyte layer with an inorganic solid electrolyte and forming a positive-electrode battery case and a negative-electrode battery case with metal sheet metal Since the periphery section of this positive-electrode battery case and a negative-electrode battery case was closed through the insulating ceramics which prepared the metalization section in the front face, the thermal resistance of the closure section of a battery case improves, and the large operational temperature range of all solid-state lithium cell original and high safety can be realized.

[Translation done.]

*** NOTICES ***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
3. In the drawings, any words are not translated.

TECHNICAL PROBLEM

[Description of the Prior Art] The need of the cell as the power source is also increasing quickly with remarkable development of the recent years of the pocket device represented by a cellular phone and the personal computer. Since an atomic weight is a cell using a small lithium with big ionization energy, especially a lithium cell is briskly studied as a cell which can obtain a high energy consistency, and has come to be used for large areas including the power source of a pocket device now.

[0003] Although it roughly divides into these lithium cells and there are cylindrical and a square shape in them, it has structure which the positive electrode and the negative electrode inserted the electrode group wound through the separator into the battery case can, poured all in there, and obturated the organic electrolytic solution.

[0004] Generally in the lithium cell, the cobalt acid lithium (LiCoO_2) and the manganic acid lithium (LiMn_2O_4) are used as positive active material. Carbon materials, such as corks and a carbon fiber, are used for the negative-electrode active material. This LiCoO_2 and LiMn_2O_4 Charge and discharge voltage is about 4V. On the other hand, the charge and discharge voltage of a carbon material is the 0V neighborhood. Therefore, the lithium cell has attained the high voltage beyond nominal-voltage 3.5V by combining these positive active material and negative-electrode active materials.

[0005] However, since these lithium cells are using the inflammable high low-boiling point organic solvent for an electrolyte, its operating temperature range is narrow and they have the problem that it cannot be used, at the elevated temperature exceeding especially 60 degrees C. Furthermore, if rapid generation of heat takes place at the time of abnormalities, such as overcharge and a short circuit, it is inherent in the danger of resulting in emitting smoke, a burst, or ignition.

[0006] Then, in order to solve the problem on these insurance, development of all the solid-state lithium cells excellent in the thermal resistance using the inorganic solid electrolyte which consists of noncombustible inorganic solid materials, and dependability is furthered. As an example of the lithium cell which used the inorganic solid electrolyte for the electrolyte, there is a thing using sulfide glass as a solid electrolyte so that it may be indicated by JP,11-7942,A, for example.

[0007] However, all the solid-state lithium cells indicated by JP,11-7942,A use for sheathing the cell case of a coin mold or a carbon button mold by which caulking obturation is carried out through the gasket made of resin in the conventional obturation section, and these can never say that thermal resistance is high, and cannot secure the large operational temperature range and large safety which are the features of the cell using a solid electrolyte.

[0008] Moreover, although pasting up and obturating a metal battery case through thermal melting arrival nature resin is proposed by the film cell or the card cell so that it may be indicated by JP,7-6743,A and JP,8-83596,A, for example, now, thermal resistance will fall more than a gasket.

[0009] This invention is made in view of the trouble of the above conventional lithium cells, and since the thermal resistance of a cell component is low, it aims at offering the lithium cell which canceled the trouble of the conventional lithium cell that safety is low.

*** NOTICES ***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

MEANS

[Means for Solving the Problem] In order to attain the above-mentioned purpose, the lithium cell of this invention In the lithium cell enclosed in the battery case which an electrolyte layer is made to intervene between a positive-electrode layer and a negative-electrode layer, and consists of a positive-electrode battery case and a negative-electrode battery case While forming said positive-electrode layer and negative-electrode layer with an active material and an inorganic solid electrolyte, forming said electrolyte layer with an inorganic solid electrolyte and forming said positive-electrode battery case and negative-electrode battery case with metal sheet metal The hermetic seal of the periphery section of this positive-electrode battery case and a negative-electrode battery case was carried out through the insulating ceramics which prepared the metalization section in the front face.

[0011] It is desirable for said positive active material and a negative-electrode active material to consist of a transition-metals oxide in the above-mentioned lithium cell.

[0012] Moreover, it is desirable for said metal sheet metal to consist in the above-mentioned lithium cell of either stainless steel, aluminum, nickel, copper, covar, 42 alloys, titanium or an aluminium alloy.

[0013] Moreover, it is desirable to form the confrontation section with the electrode layer of said positive-electrode battery case and/or a negative-electrode battery case in a concave in the above-mentioned lithium cell.

[Translation done.]

*** NOTICES ***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

OPERATION

[Function] As mentioned above, if a battery case is formed with metal sheet metal and a hermetic seal is carried out through the insulating ceramics, all components will have thermal resistance and incombustibility, and will not result in emitting smoke, a burst, or ignition by rapid generation of heat, either, and safety will be secured.

[0015] Moreover, if positive active material and a negative-electrode active material are used as transition-metals oxide, also when a cell overcharges, a deposit of a metal lithium will not take place, but the dependability of a cell will improve.

[0016] Furthermore, when stainless steel, aluminum, nickel, copper, covar, 42 alloys, titanium, or an aluminium alloy is used for the metallic thin plate made into a battery case, the metal plate of an electrode group stowage was fabricated to the concave in addition and it is heated by welding at the time of the closure, the residual stress which a battery case does not cause too much deformation and is applied to the closure section can be eased, and the dependability of the closure section can be raised.

[0017]

[Embodiment of the Invention] Hereafter, the operation gestalt of the lithium cell of this invention is explained. Drawing 1 is the sectional view showing the example of a configuration of the lithium cell concerning this invention. For an electrolyte layer and 3, as for a positive-electrode battery case and 5, in drawing 1, a negative-electrode layer and 4 are [1 / a positive-electrode layer and 2 / a negative-electrode battery case and 6] the closure sections. Drawing 2 is the expanded sectional view of the closure section of the lithium cell concerning this invention. For the insulating ceramics and 8, as for a nickel-plating layer and 10, in drawing 2, the metalization section and 9 are [7 / a silver solder layer and 11] seal frames.

[0018] The positive-electrode layer 1 and the negative-electrode layer 3 mainly consist of an active material and an inorganic solid electrolyte. The following transition-metals oxides are mentioned as an active material used for the positive-electrode layer 1 and the negative-electrode layer 3. For example, a lithium manganese multiple oxide, a manganese dioxide, lithium nickel complex oxide, a lithium cobalt multiple oxide, a lithium nickel cobalt multiple oxide, a lithium vanadium multiple oxide, a lithium titanium multiple oxide, titanium oxide, niobium oxide, a vanadium oxide, tungstic oxide, etc. and those derivatives are mentioned. Here, what shows more **** potential to a positive electrode for what a clear distinction does not have in positive active material and a negative-electrode active material, compares the charge and discharge potential of two kinds of transition-metals oxides, and shows electropositive potential more can be used for a negative electrode, respectively, and the cell of the electrical potential difference of arbitration can be constituted. If transition-metals oxide is used for positive active material and a negative-electrode active material, also when a cell overcharges, a deposit of a metal lithium will not take place, but the dependability of a cell will improve.

[0019] To the inorganic solid electrolyte used for the positive-electrode layer 1, the negative-electrode layer 3, and the electrolyte layer 2 Li_{1.3}Al_{0.3}Ti_{1.7}O₃ [for example,] (PO₄)₃Li_{3.6}germanium 0.6V_{0.4}O₄ etc. -- a crystalline substance solid electrolyte -- 30LiI-41Li₂O-29P₂O₅ 40Li(s)O₃-35B₂O₃-25LiNbO₃, Oxide system noncrystalline solid electrolytes, such as 10Li₂O-25B₂O₃-15SiO₂-50ZnO, 45LiI-37Li₂S-18P₂S₅ Li₃PO₄-63Li₂S-36SiS₂ etc. --

a sulfide system noncrystalline solid electrolyte etc. can be mentioned.

[0020] The positive-electrode layer 1 consists of the porous body or precise object which added and carried out pressing of the shaping assistant to positive active material and an inorganic solid electrolyte, and heat-treated it to them, and the negative-electrode layer 3 consists of the porous body or precise object which used as the active material the transition-metals oxide which has **** charge and discharge potential rather than the charge and discharge potential of the positive active material in the positive-electrode layer 1.

[0021] In order to produce the positive-electrode layer 1 and the negative-electrode layer 3, make the water or the solvent in which the shaping assistant was dissolved distribute (1) active material and an inorganic solid electrolyte, and a slurry is prepared. How to heat-treat what carried out pressing and was judged after applying this slurry on the base material film and drying. Or add and corn a direct or shaping assistant and the mixture of (2) active materials and an inorganic solid electrolyte is fed into metal mold. After carrying out pressing of the approach of heat-treating after carrying out pressing with a press machine, and the mixture which carried out (3) granulation with a roll press machine and processing it in the shape of a sheet, the approach of cutting out and heat-treating the sheet etc. is used. Even if the granulation of (2) and (3) is dry type granulation which does not use a solvent even if it is the wet agglomeration which corns from the slurry stated by the approach of (1), it is not cared about.

[0022] The electrolyte layer 2 is producible by producing and heat-treating a Plastic solid only from an inorganic solid electrolyte and a shaping assistant like above-mentioned process (1) - (3).

[0023] As an approach of producing the electrode group which comes to carry out the laminating of the positive-electrode layer 1, the above-mentioned negative-electrode layer 3, and the above-mentioned electrolyte layer 2 How to carry out the specified quantity laminating of each class which heat-treated according to the individual and was used as the porous body or the precise object, and heat-treat it through the electrolyte layer 2 before heat-treating the approach of carrying out a specified quantity laminating, and the positive-electrode layer 1 and the negative-electrode layer 3 after heat treatment, the approach of carrying out the specified quantity laminating of each class before heat treatment, bundling it up, and heat-treating it, etc. can be considered.

[0024] Anyway, as an usable shaping assistant, one sort or two sorts or more of mixture, such as polytetrafluoroethylene, polyacrylic acid, a carboxymethyl cellulose, polyvinylidene fluoride, polyvinyl alcohol, diacetyl cellulose, hydroxypropylcellulose, the poly butyral, polyvinyl chloride, and a polyvinyl pyrrolidone, is mentioned here, for example.

[0025] As a base material film, metallic foils, such as resin films, such as polyethylene terephthalate, polypropylene, polyethylene, and polytetrafluoroethylene, aluminum, stainless steel, and copper, etc. are usable, for example.

[0026] The metal sheet metal used for the positive-electrode battery case 4 and the negative-electrode battery case 5 is limited to neither the manufacture approach nor especially purity that what is necessary is just stainless steel, aluminum, nickel, copper, covar, 42 alloys, titanium, or an aluminium alloy. Moreover, the adjustment of a coefficient of thermal expansion can be taken, and it is satisfactory even if the classes of metallic thin plate used for a positive-electrode battery case and a negative-electrode battery case differ through the insulating ceramics 7, if a hermetic seal is possible. Suitable thickness should be chosen from the field of the reinforcement as the existence and the sheathing material of a pinhole although it is desirable to use a thin thing from a viewpoint of the energy density of a cell as for board thickness. For example, in the case of covar, it is desirable to be referred to as 30 micrometers or more. It is desirable to be referred to as 500 micrometers or less on the other hand in the thicker one from a viewpoint of constraint by the closure approach, the bonding strength of the closure section, or energy density.

[0027] The confrontation section with the electrode layer of the positive-electrode battery case 4 may be fabricated to a concave, and the existing conventional technique can be used for this concave shaping approach. For example, press working of sheet metal by shaping metal mold is common. That a configuration is seen from an electrode group stowage and should just be a

concave, although neither the depth nor especially a dimension is limited, it should make the dimension and the configuration where an electrode group and a battery case 4 can contact in consideration of the thickness of an electrode group, and the thickness of the insulating ceramics 7 in a field. Moreover, in case it fabricates depending on the shaping approach, a concave electrode group stowage serves as a trapezoid, or it is satisfactory in any way by considering as the design of the arbitration which it may be more convenient to establish a curved surface in a flection, and was suitable for the shaping approach.

[0028] As insulating ceramics 7 concerning this invention, although an alumina, a steatite, a mullite, zircon, a glass ceramic, aluminum nitride, etc. can be used, if a price, an electrical property, a mechanical property, etc. are taken into consideration, the alumina of 90% or more of purity which uses an aluminum oxide (aluminum 2O3) as a principal component is suitable.

[0029] In order to produce the insulating ceramics 7 which formed the metalization section 8 in the front face, an annular alumina sintered compact can be first produced from an alumina raw material, then metallizing of Mo and Mn can be carried out, nickel plating can be performed to the front face, and the approach of carrying out silver soldering of the metal which can be welded to battery cases 4 and 5 can be used.

[0030] In order to produce the annular alumina sintered compact 7 from an alumina raw material (1) Make the water or the solvent in which the shaping assistant was dissolved distribute alumina raw material powder, and a slurry is prepared. How to sinter what was judged annularly, after applying this slurry on a base material film and drying. Or add and corn a direct or shaping assistant and (2) alumina raw materials are fed into metal mold. After carrying out pressing of the approach of sintering after carrying out pressing with a press machine, and the mixture which carried out (3) granulation with a roll press machine and processing it in the shape of a sheet, the approach of cutting out the sheet annularly and sintering it etc. is used. Even if the granulation of (2) and (3) is dry type granulation which does not use a solvent even if it is the wet agglomeration which corns from the slurry stated by the approach of (1), it is not cared about.

[0031] Next, the approach of often mixing both, adding a binder using the impalpable powder of Mo and Mn for metallizing both sides of the above-mentioned alumina sintered compact 7, considering as the shape of a paste, applying to the alumina sintered compact front face which performed surface polish and surface treatment beforehand, carrying out elevated temperature baking all over the hydrogen furnace of a humidification ambient atmosphere, and making a metallized layer (metalization section) 8 forming can be use.

[0032] Electrolysis plating and an electroless deposition method can be used for formation of the nickel-plating layer 9. In addition, it is desirable to perform sintering, in order to raise adhesion with the metallized layer 8 of a substrate, while carrying out eburnation of the nickel-plating layer 9.

[0033] Junction in the seal frame 11 and the nickel-plating layer 9 which consist of a metal is possible at the thing which will shine through the silver solder layer 10 and which is attached and done. However, since suitable wax material is selected by the class of metal used for a seal frame, the silver solder layer 10 is not necessarily silver solder.

[0034] In the approach of producing the insulating ceramics 7 which formed the metalization section 8 in the front face The conductive paste of refractory metals, such as Mo and W, is screen-stenciled to the alumina Plastic solid which is not calcinated other than the above-mentioned metallizing method. Calcinate, after printing thickly the coincidence calcinating method calcinated collectively and the conductive paste which consists of a metal powder, low melting glass, and an organic binder by screen-stencil on an alumina sintered compact, and the organic substance is removed. There is physical vapor deposition in which a metal layer is made to form with physical vapor deposition which makes a metal fix with low melting glass, such as a thick-film method, vacuum deposition, and sputtering.

[0035] CO2 of existing [welding / with a seal frame 11 and a battery case] I will use the alloy of the micro parallel seam conjugation method which is a kind of laser-welding methods, such as gas laser and an YAG laser, and a resistance welding method, and a Pb-Sn system and an Au-Sn system, and law can be applied.

[0036] That what is necessary is just the structure contained by the metal sheet metal battery case to which the closure of the electrode group to which the laminating of the positive-electrode layer 1, the electrolyte layer 2, and the negative-electrode layer 3 which consist of an inorganic solid material was carried out was carried out through the insulating ceramics 7, even if the lithium cell of this invention is a primary cell and it is a rechargeable battery, it does not interfere. Moreover, an electrolyte should just be an inorganic solid material which has ion conductivity, and also any, such as rectangular heads, such as a card mold, a film mold, and a flat mold, a trigonum, and a round shape, are sufficient as a cell configuration.

[Translation done.]

*** NOTICES ***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

EXAMPLE

[Example] Hereafter, this invention is explained in more detail based on an example.

[0038] The [example 1] lithium hydroxide and the manganese dioxide were mixed so that the mole ratio of Li and Mn might be set to 1:2, by carrying out heating baking of this mixture at 700 degrees C among atmospheric air for 15 hours, the lithium manganese multiple oxide (LiMn₂O₄) was prepared, and this was made into positive active material. Next, the lithium hydroxide and the titanium dioxide were mixed so that the mole ratio of Li and Ti might be set to 4:5, and by carrying out heating baking of this mixture at 750 degrees C in atmospheric air for 15 hours, the lithium titanium multiple oxide (Li₄Ti₅O₁₂) was prepared, and it considered as the negative-electrode active material.

[0039] This LiMn₂O₄ 10Li₂O-25B-2O₃-15SiO₂-50ZnO was blended dryly by the weight ratio 80:20, and it considered as mixed powder each of Li₄Ti₅O₁₂, an inorganic solid electrolyte, and here. In addition, toluene was added further and the slurry was prepared so that the polyvinyl butyral of a shaping assistant might be set to 10 by the weight ratio to this mixed powder 100. Pressurization compression molding of what was made to dry after applying this slurry on a polyethylene terephthalate (PET) film, and was fabricated in the shape of a sheet was carried out by the roll press, the positive electrode was used into the thickness of 0.5mm, and the negative electrode was used as the sheet with a thickness of 0.5mm. Each sheet was pierced with metal mold and sheet-like the positive electrode and negative-electrode Plastic solid of 20mm angle were acquired.

[0040] Next, the polyvinyl butyral of a shaping assistant was mixed with the inorganic solid electrolyte by the weight ratio 100:10, toluene was added further, the slurry was prepared, and the Plastic solid of 20mm angle and the shape of a sheet with a thickness of 0.2mm was produced by fabricating the same on a PET film and judging.

[0041] The laminating of the above-mentioned positive-electrode layer 1 and the negative-electrode layer 3 was carried out through the electrolyte layer 2, package heat treatment of this was carried out at 550 degrees C among atmospheric air, and 18mm angle and the electrolyte layer 2 with a thickness of 0.85mm were produced. The metallic thin plate which judged the covar material with a same thickness of 0.1mm which performed nickel plating on 25mm square was used for the positive-electrode battery case 4 and the negative-electrode battery case 5. However, what fabricated the electrode group stowage by press forming to the concave beforehand was used for the positive-electrode battery case. Width of face of 5mm which carried out silver soldering of the seal frame 10 made from covar by the metallizing method beforehand, and the thing which welded the annular insulating ceramics 7 with a thickness of 0.3mm with the parallel seam conjugation method were used for the negative-electrode battery case 5.

[0042] After having arranged the electrode group in the center of the negative-electrode battery case 5, the card mold lithium cell which put the positive-electrode battery case 4, closed the periphery section of the positive-electrode battery case 4 with the micro parallel seam conjugation method, and was shown in drawing 1 was produced.

[0043] The card mold lithium cell was assembled like the example 1 except having produced the [example 2] positive-electrode battery case 4, the negative-electrode battery case 5, and the

seal frame 11 by stainless steel 304.

[0044] It contained to the space surrounded by the polyolefin resin which has an adhesive property to the covar which is a battery case about the electrode group produced like the [example 1 of comparison] example 1, and this covar, and which was fabricated annularly, and it heated, pressurizing with a 140-degree C hot platen, the battery case was sealed, and the card mold lithium cell was produced.

[0045] The card mold lithium cell was assembled like the example 1 except having used for the [example 2 of comparison] positive-electrode battery case the metallic thin plate made from covar which has not processed the electrode group stowage into a concave.

[0046] The purpose which evaluates thermal resistance using the cell produced in the above-mentioned examples 1 and 2 and the examples 1 and 2 of a comparison estimated capacity degradation by elevated-temperature neglect. After evaluation checked that left it in the 100 or 125,150,175,200-degree C thermostat for 100 hours, took out out of the tub, and the temperature of a cell had become a room temperature after preparing each five cells and carrying out a full charge to 2.9V with the current value of the rate of 10 time amount at a room temperature first, it was performed by the approach of carrying out constant-current discharge to 1.5V with the current value of the same rate of 10 time amount as charge, calculating discharge capacity, and searching for the charge-and-discharge effectiveness over a previous charge capacity. The result is as being shown in Table 1.

[0047]

[Table 1]

	充放電効率 (%)				
	100℃	125℃	150℃	175℃	200℃
実施例 1	98	98	98	98	98
実施例 2	98	98	98	98	98
比較例 1	98	92	31	14	0
比較例 2	98	71	16	0	0

$$\text{充放電効率} (\%) = (\text{放電容量} / \text{充電容量}) \times 100$$

[0048] The decline in the charge-and-discharge effectiveness by elevated-temperature neglect is not seen at all, but its effectiveness of this invention is remarkable in the range to 200 degrees C evaluated by the example to the example of a comparison so that clearly from Table 1. Since the cause that charge-and-discharge effectiveness fell in the range of 150 degrees C or more in the example 1 of a comparison has the low thermal resistance of resin, it is presume to be what resin fused, and moisture invaded in the cell from the sealing section, reacted with the lithium in an active material, and caused irreversible capacity degradation during elevated-temperature neglect. Moreover, since the residual stress at the time of sealing could not be borne, but the crack arose and moisture invaded in the cell when the sealing section was heated, since the electrode group stowage of a battery case was not fabricated to a concave, the capacity fall of the example 2 of a comparison is considered. However, the thickness of an electrode group is thin, or since the residual stress produced in the sealing section becomes small when the thickness of the metallic thin plate of a battery case is thin, it is thought that a crack is not generated.

[0049] Therefore, invasion of moisture is prevented by welding the battery case which consists of the product made from a metallic thin plate which does not have a pinhole through the insulating ceramics, and the large operational temperature range of all solid-state lithium cell original and high safety can be realized. In addition, although an example did not indicate the example of active materials other than metal [other than covar and stainless steel] and LiMn₂O₄, and Li₄Ti₅O₁₂, all are the existing ingredients and it is clear that the same effectiveness is acquired.

*** NOTICES ***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the sectional view of the lithium cell concerning this invention.

[Drawing 2] It is the expanded sectional view of the closure section of the lithium cell concerning this invention.

[Description of Notations]

1 [-- A positive-electrode battery case, 5 / -- A negative-electrode battery case, 6 / -- Low melting glass, 7 / -- The insulating ceramics, 8 / -- The metalization section, 9 / -- A nickel-plating layer, 10 / -- A silver solder layer, 11 / -- Seal frame] -- A positive-electrode layer, 2 -- An electrolyte layer, 3 -- A negative-electrode layer, 4

[Translation done.]

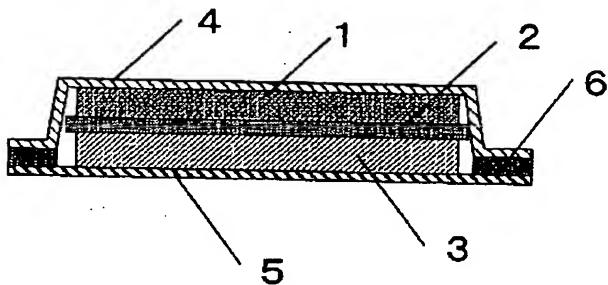
* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

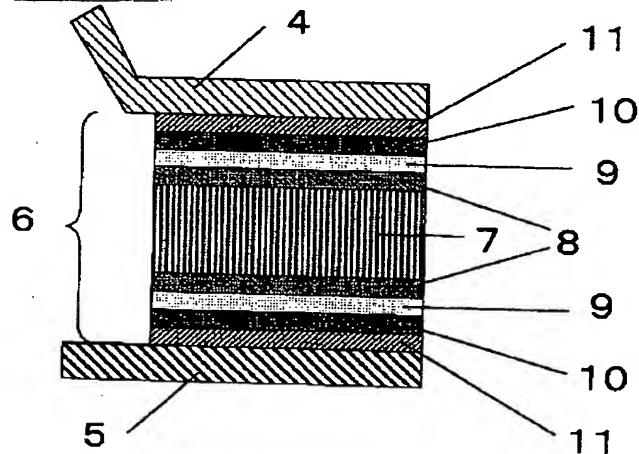
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]



[Drawing 2]



[Translation done.]

(19)日本国特許庁 (JP)

(12) 公開特許公報 (A)

(11)特許出願公開番号

特開2001-43892

(P2001-43892A)

(43)公開日 平成13年2月16日(2001.2.16)

(51)Int.Cl.⁷

H 0 1 M 10/36
6/18

識別記号

F I

H 0 1 M 10/36
6/18

マークコード*(参考)

A 5 H 0 2 4
A 5 H 0 2 9

審査請求 未請求 請求項の数4 O L (全 6 頁)

(21)出願番号 特願平11-214846

(22)出願日 平成11年7月29日(1999.7.29)

(71)出願人 000006633

京セラ株式会社

京都府京都市伏見区竹田烏羽殿町6番地

(72)発明者 三島 洋光

京都府相楽郡精華町光台3丁目5番地 京セラ株式会社中央研究所内

(72)発明者 馬込 伸二

京都府相楽郡精華町光台3丁目5番地 京セラ株式会社中央研究所内

(72)発明者 上村 傑彦

京都府相楽郡精華町光台3丁目5番地 京セラ株式会社中央研究所内

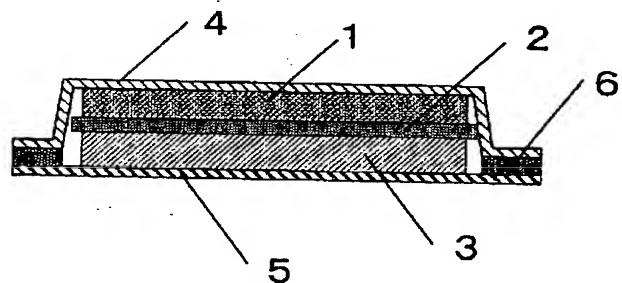
最終頁に続く

(54)【発明の名称】 リチウム電池

(57)【要約】

【課題】 電池構成材料の耐熱性が低いために安全性が低いという問題があった。

【解決手段】 正極層1と負極層3との間に電解質層2を介在させて正極電槽4と負極電槽5などで構成される電槽内に封入したリチウム電池であって、前記正極層1と負極層3とを活物質と無機固体電解質で形成し、前記電解質層2を無機固体電解質で形成し、上記正極電槽4と負極電槽5とを金属製薄版で形成すると共に、この正極電槽4と負極電槽5との周縁部を表面に金属化部8を設けた絶縁性絶縁性セラミックス7を介して気密封止した。



【特許請求の範囲】

【請求項1】 正極層と負極層との間に電解質層を介在させて正極電槽と負極電槽とで構成される電槽内に封入したリチウム電池において、前記正極層と負極層とを活物質と無機固体電解質で形成し、前記電解質層を無機固体電解質で形成し、前記正極電槽と負極電槽とを金属製薄板で形成すると共に、この正極電槽と負極電槽との周縁部を表面に金属化部を設けた絶縁性セラミックスを介して気密封止したことを特徴とするリチウム電池。

【請求項2】 前記正極活物質および負極活物質が遷移金属酸化物であることを特徴とする請求項1に記載のリチウム電池。

【請求項3】 前記金属製薄板がステンレス、アルミニウム、ニッケル、銅、コバルト、42アロイ、チタンあるいはアルミニウム合金のいずれかから成ることを特徴とする請求項1または請求項2に記載のリチウム電池。

【請求項4】 前記正極電槽および／または負極電槽の前記電極層との対峙部が凹状に形成されていることを特徴とする請求項1ないし請求項3に記載のリチウム電池。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明はリチウム電池に関し、特に電極層や電解質層が無機物から成るリチウム電池に関する。

【0002】

【従来技術および発明が解決しようとする課題】 携帯電話やパーソナルコンピュータに代表される携帯機器の近年の目覚しい発達に伴い、その電源としての電池の需要も急速に増加している。特に、リチウム電池は原子量が小さく、かつイオンエネルギーが大きなりチウムを使う電池であることから、高エネルギー密度を得ることができる電池として盛んに研究され、現在では携帯機器の電源をはじめとして広範囲に用いられるに至っている。

【0003】 これらのリチウム電池には、大きく分けて円筒型と角型があるが、いずれも正極と負極がセパレータを介して捲回された極群を電槽缶内に挿入し、そこに有機電解液を注入して封口した構造となっている。

【0004】 リチウム電池では、正極活物質としてコバルト酸リチウム (LiCoO_2) やマンガン酸リチウム (LiMn_2O_4) が一般的に用いられている。負極活物質には、コークスや炭素繊維などの炭素材料が用いられている。この LiCoO_2 や LiMn_2O_4 の充放電電圧は約 4 V である。これに対して炭素材料の充放電電圧は 0 V 付近である。したがって、これらの正極活物質と負極活物質を組み合わせることでリチウム電池は公称電圧 3.5 V 以上の高電圧を達成している。

【0005】 しかしながら、これらのリチウム電池は電解質に可燃性の高い低沸点有機溶媒を使用しているため、作動温度範囲が狭く、特に 60°C を超える高温では

使用できないという問題がある。さらに、過充電や短絡といった異常時に急激な発熱が起こると発煙や破裂や発火に至る危険性を内在している。

【0006】 そこで、これら安全上の問題を解決するために、不燃性の無機固体材料で構成される無機固体電解質を用いた耐熱性、信頼性に優れた全固体リチウム電池の開発が進められている。電解質に無機固体電解質を用いたリチウム電池の例としては、例えば特開平11-7942号公報に開示されるように、固体電解質として硫化物ガラスを用いたものがある。

【0007】 しかしながら、特開平11-7942号公報で開示される全固体リチウム電池は外装に従来の封口部で樹脂製のガスケットを介してかしめ封口されるコイン型やボタン型の電池ケースを用いており、これらは決して耐熱性が高いとはいえない。固体電解質を用いた電池の特長である広い動作温度範囲と安全性を確保することはできない。

【0008】 また、フィルム電池やカード電池では、例えば特開平7-6743号公報や特開平8-83596号公報に開示されるように、熱融着性樹脂を介して金属製電槽を接着して封口することが提案されているが、これではガスケット以上に耐熱性が低下してしまう。

【0009】 本発明は上述のような従来のリチウム電池の問題点に鑑みてなされたものであり、電池構成材料の耐熱性が低いために安全性が低いという従来のリチウム電池の問題点を解消したリチウム電池を提供することを目的とする。

【0010】

【課題を解決するための手段】 上述の目的を達成するために、本発明のリチウム電池は、正極層と負極層との間に電解質層を介在させて正極電槽と負極電槽とで構成される電槽内に封入したリチウム電池において、前記正極層と負極層とを活物質と無機固体電解質で形成し、前記電解質層を無機固体電解質で形成し、前記正極電槽と負極電槽とを金属製薄板で形成すると共に、この正極電槽と負極電槽との周縁部を表面に金属化部を設けた絶縁性セラミックスを介して気密封止した。

【0011】 上記リチウム電池では、前記正極活物質および負極活物質が遷移金属酸化物から成ることが望ましい。

【0012】 また、上記リチウム電池では、前記金属製薄板がステンレス、アルミニウム、ニッケル、銅、コバルト、42アロイ、チタンあるいはアルミニウム合金のいずれかから成ることが望ましい。

【0013】 また、上記リチウム電池では、前記正極電槽および／または負極電槽の電極層との対峙部が凹状に形成されていることが望ましい。

【0014】

【作用】 上記のように、電槽を金属製薄板で形成して絶縁性セラミックスを介して気密封止すると、構成材料全

てが耐熱性と不燃性を有することとなり、急激な発熱によっても発煙や破裂や発火に至ることがなく、安全性が確保される。

【0015】また、正極活物質と負極活物質を遷移金属酸化物とすると、電池が過充電された場合にも金属リチウムの析出が起ららず、電池の信頼性が向上する。

【0016】さらに、電槽とする金属薄板にステンレス、アルミニウム、ニッケル、銅、コバルト、42アロイ、チタンあるいはアルミニウム合金を用い、加えて極群収納部の金属板を団状に成形すると、封止時に溶接によって加熱されたときに、電槽が過度の変形を起こすことなく、封止部にかかる残留応力を緩和して封止部の信頼性を向上させることができる。

【0017】

【発明の実施の形態】以下、本発明のリチウム電池の実施形態について説明する。図1は、本発明に係るリチウム電池の構成例を示す断面図である。図1において、1は正極層、2は電解質層、3は負極層、4は正極電槽、5は負極電槽、6は封止部である。図2は、本発明に係るリチウム電池の封止部の拡大断面図である。図2において、7は絶縁性セラミックス、8は金属化部、9はニッケルメッキ層、10は銀ろう層、11はシールフレームである。

【0018】正極層1および負極層3は主として活物質と無機固体電解質で構成される。正極層1および負極層3に用いる活物質としては、次のような遷移金属酸化物が挙げられる。例えば、リチウムマンガン複合酸化物、二酸化マンガン、リチウムニッケル複合酸化物、リチウムコバルト複合酸化物、リチウムニッケルコバルト複合酸化物、リチウムバナジウム複合酸化物、リチウムチタン複合酸化物、酸化チタン、酸化ニオブ、酸化バナジウム、酸化タングステンなどとそれらの誘導体が挙げられる。ここで、正極活物質と負極活物質には明確な区別ではなく、2種類の遷移金属酸化物の充放電電位を比較してより貴な電位を示すものを正極に、より卑な電位を示すものを負極にそれぞれ用いて任意の電圧の電池を構成することができる。正極活物質と負極活物質に遷移金属酸化物を用いると、電池が過充電された場合にも金属リチウムの析出が起ららず、電池の信頼性が向上する。

【0019】正極層1、負極層3および電解質層2に用いられる無機固体電解質には、例えばLi_{1.3}Al_{0.3}

Ti_{1.7}(PO₄)₃やLi_{1.6}Ge_{0.6}V_{0.4}O₄などの結晶質固体電解質、30LiI-41Li₂O-29P₂O₅や40Li₂O-35B₂O₃-25LiNbO₃、10Li₂O-25B₂O₃-15SiO₂-50ZnOなどの酸化物系非晶質固体電解質、45LiI-37Li₂S-18P₂S₃やLi₃PO₄-63Li₂S-36SiS₂などの硫化物系非晶質固体電解質などを挙げることができる。

【0020】正極層1は、正極活物質と無機固体電解質

に成形助剤を加えて加圧成形して熱処理した多孔質体あるいは緻密体から成り、負極層3は、正極層1中の正極活物質の充放電電位よりも卑な充放電電位を有する遷移金属酸化物を活物質とした多孔質体あるいは緻密体からなる。

【0021】正極層1および負極層3を作製するには、

(1) 活物質と無機固体電解質を成形助剤を溶解させた水もしくは溶剤に分散させてスラリーを調製し、このスラリーを基材フィルム上に塗布して乾燥した後、加圧成形して裁断したものを熱処理する方法、あるいは(2) 活物質と無機固体電解質の混合物を直接あるいは成形助剤を加えて造粒して金型に投入し、プレス機で加圧成形した後、熱処理する方法、(3) 造粒した混合物をロールプレス機で加圧成形してシート状に加工した後、そのシートを裁断して熱処理する方法などが用いられる。

(2)、(3)の造粒は、(1)の方法で述べたスラリーから造粒する湿式造粒であっても溶剤を用いない乾式造粒であっても構わない。

【0022】電解質層2は、上記製法(1)～(3)と同様にして無機固体電解質と成形助剤のみから成形体を作製し、熱処理することによって作製することができる。

【0023】上述の正極層1、負極層3および電解質層2を積層してなる極群を作製する方法としては、個別に熱処理して多孔質体あるいは緻密体とした各層を所定量積層する方法や、熱処理後の正極層1と負極層3を熱処理前の電解質層2を介して所定量積層して熱処理する方法や、熱処理前の各層を所定量積層して一括して熱処理する方法などが考えられる。

【0024】いずれにしても、ここで使用可能な成形助剤としては、例えばポリテトラフルオロエチレン、ポリアクリル酸、カルボキシメチルセルロース、ポリフッ化ビニリデン、ポリビニルアルコール、ジアセチルセルロース、ヒドロキシプロピルセルロース、ポリブチラル、ポリビニルクロライド、ポリビニルピロリドンなどの1種もしくは2種以上の混合物が挙げられる。

【0025】基材フィルムとしては、例えばポリエチレンテレフタレート、ポリプロピレン、ポリエチレン、ポリテトラフルオロエチレンなどの樹脂フィルム、アルミニウム、ステンレス、銅などの金属箔などが使用可能である。

【0026】正極電槽4と負極電槽5に用いる金属製薄板は、ステンレス、アルミニウム、ニッケル、銅、コバルト、42アロイ、チタンあるいはアルミニウム合金であればよく、製造方法や純度には特に限定されない。また、熱膨張係数の整合性がとれ、絶縁性セラミックス7を介して気密封止可能であれば正極電槽と負極電槽に用いる金属薄板の種類が異なっても問題はない。板厚は、電池のエネルギー密度の観点から薄いものを用いるのが望ましいが、ピンホールの有無や外装材としての強度の

面から適当な厚みが選択されるべきである。例えばコバルトの場合、 $30\text{ }\mu\text{m}$ 以上とすることが望ましい。一方、厚いほうでは、封止方法による制約や封止部の接合強度やエネルギー密度の観点から $500\text{ }\mu\text{m}$ 以下とするのが好ましい。

【0027】正極電槽4の電極層との対峙部を凹状に成形してもよく、この凹状の成形方法には既存の従来技術を用いることができる。例えば成形金型によるプレス加工が一般的である。形状は、極群収納部から見て凹状であれば良く、深さや寸法は特に限定されないが、極群の厚みと絶縁性セラミックス7の厚みを考慮して極群と電槽4が面で接触できる寸法、形状にすべきである。また、成形方法によっては成形する際に凹状の極群収納部が台形となったり、屈曲部に曲面を設けたほうが好都合な場合があり、成形方法に適した任意の設計とすることで何ら問題はない。

【0028】本発明にかかる絶縁性セラミックス7としては、アルミナ、ステアタイト、ムライト、ジルコン、ガラスセラミック、窒化アルミニウムなどを用いることができるが、価格と電気的性質、機械的性質などを考慮すると酸化アルミニウム(Al_2O_3)を主成分とする純度90%以上のアルミナが好適である。

【0029】表面に金属化部8を設けた絶縁性セラミックス7を作製するには、まずアルミナ原料から環状のアルミナ焼結体を作製し、次にMo、Mnをメタライズして、その表面にニッケルメッキを施し、電槽4、5と溶接可能な金属を銀ろう付けする方法を用いることができる。

【0030】アルミナ原料から環状のアルミナ焼結体7を作製するには、(1)アルミナ原料粉を成形助剤を溶解させた水もしくは溶剤に分散させてスラリーを調製し、このスラリーを基材フィルム上に塗布して乾燥した後、環状に裁断したものを焼結する方法、あるいは

(2)アルミナ原料を直接あるいは成形助剤を加えて造粒して金型に投入し、プレス機で加圧成形した後、焼結する方法、(3)造粒した混合物をロールプレス機で加圧成形してシート状に加工した後、そのシートを環状に裁断して焼結する方法などが用いられる。(2)、

(3)の造粒は、(1)の方法で述べたスラリーから造粒する湿式造粒であっても溶剤を用いない乾式造粒であっても構わない。

【0031】次に、上述のアルミナ焼結体7の両面を金属化するにはMoとMnの微粉末を用い、両者をよく混合し、バインダーを加えてペースト状とし、予め表面研磨および表面処理を施したアルミナ焼結体表面に塗布し、加湿雰囲気の水素炉中で高温焼成してメタライズ層(金属化部)8を形成させる方法を用いることができる。

【0032】ニッケルメッキ層9の形成には電解メッキ法や無電解メッキ法を用いることができる。なお、ニッ

ケルメッキ層9を緻密化すると共に下地のメタライズ層8との密着性を上げるためにシンタリングを行うのが好ましい。

【0033】金属から成るシールフレーム11とニッケルメッキ層9との接合は、銀ろう層10を介してろう付けすること可能である。ただし、銀ろう層10は、シールフレームに用いる金属の種類によって適当なろう材が選定されるので必ずしも銀ろうとは限らない。

【0034】表面に金属化部8を設けた絶縁性セラミックス7を作製する方法には、上述のメタライズ法以外に未焼成のアルミナ成形体にMoやWなどの高融点金属の導体ペーストをスクリーン印刷し、一括して焼成する同時焼成法や、アルミナ焼結体上にスクリーン印刷で金属粉と低融点ガラスと有機バインダーから成る導体ペーストを厚く印刷した後に焼成して有機物を除去し、低融点ガラスによって金属を固着させる厚膜法や、真空蒸着やスパッタリングなどの物理蒸着法によって金属層を形成させる物理蒸着法がある。

【0035】シールフレーム11と電槽との溶接には、既存のCO₂ガスレーザやYAGレーザなどのレーザ溶接法や、抵抗溶接法の一種であるマイクロパラレルシーム接合法や、Pb-Sn系、Au-Sn系の合金を使用したろう付け法が適用可能である。

【0036】本発明のリチウム電池は、無機固体材料からなる正極層1、電解質層2および負極層3が積層された極群が絶縁性セラミックス7を介して封止された金属製薄板電槽に収納された構造であればよく、一次電池であっても二次電池であっても差し支えない。また、電解質はイオン伝導性を有する無機固体材料であればよいほか、電池形状はカード型、フィルム型および扁平型などの四角や三角、円形などいずれでもよい。

【0037】

【実施例】以下、本発明を実施例に基づいてさらに詳しく説明する。

【0038】【実施例1】水酸化リチウムと二酸化マンガンをLiとMnのモル比が1:2となるように混合し、この混合物を大気中、700°Cで15時間加熱焼成することによってリチウムマンガン複合酸化物(Li₁Mn₂O₄)を調製し、これを正極活物質とした。次に、水酸化リチウムと二酸化チタンをLiとTiのモル比が4:5となるように混合し、この混合物を大気中の750°Cで15時間加熱焼成することによってリチウムチタン複合酸化物(Li₁Ti₅O₁₂)を調製して負極活物質とした。

【0039】このLiMn₂O₄とLi₁Ti₅O₁₂のそれぞれと無機固体電解質、ここでは10Li₂O-25B₂O₃-15SiO₂-50ZnOとを重量比80:20で乾式混合し混合粉とした。この混合粉100に対して成形助剤のポリビニルブチラールが重量比で10となるように加え、さらにトルエンを加えてスラリー

を調製した。このスラリーをポリエチレンテレフタレート(PET)フィルム上に塗布した後に乾燥させてシート状に成形したものをロールプレスによって加圧圧縮成形して、正極は厚み0.5mm、負極は厚み0.5mmのシートとした。それぞれのシートを金型で打ち抜いて20mm角のシート状の正極および負極成形体を得た。
【0040】次に、無機固体電解質と成形助剤のポリビニルブチラールを重量比100:10で混合し、さらにトルエンを加えてスラリーを調製し、PETフィルム上に同じく成形して裁断することで、20mm角、厚み0.2mmのシート状の成形体を作製した。

【0041】上記正極層1と負極層3を電解質層2を介して積層し、これを大気中、550°Cで一括熱処理して18mm角、厚み0.85mmの電解質層2を作製した。正極電槽4と負極電槽5にはニッケルメッキを施した同じ厚み0.1mmのコバール材を25mm角に裁断した金属薄板を用いた。ただし、正極電槽には予めプレス成形で極群収納部を凹状に成形したものを用いた。負極電槽5には、予めコバール製のシールフレーム10をメタライズ法によって銀ろう付けした幅5mm、厚み0.3mmの環状の絶縁性セラミックス7をパラレルシーム接合法によって溶接しておいたものを用いた。

【0042】負極電槽5の中央に極群を配置した後に正極電槽4を被せて正極電槽4の周縁部をマイクロバラルシーム接合法によって封止して図1に示したカード型リチウム電池を作製した。

10

20

* 【表1】

	充放電効率(%)				
	100℃	125℃	150℃	175℃	200℃
実施例1	98	98	98	98	98
実施例2	98	98	98	98	98
比較例1	98	92	31	14	0
比較例2	98	71	16	0	0

$$\text{充放電効率(%)} = (\text{放電容量} / \text{充電容量}) \times 100$$

【0048】表1から明らかなように、比較例に対して実施例では評価した200°Cまでの範囲において高温放置による充放電効率の低下は全く見られず、本発明の効果が顕著である。比較例1で150°C以上の範囲において充放電効率が低下した原因是、樹脂の耐熱性が低いために、高温放置中に樹脂が溶融して封着部から水分が電池内に侵入して活物質中のリチウムと反応して不可逆な容量劣化を引き起こしたものと推定される。また、比較例2の容量低下は、電槽の極群収納部を凹状に成形していないために、封着部が加熱されたときに封着時の残留応力に耐えられず、割れが生じて水分が電池内に侵入したためと考えられる。ただし、極群の厚みが薄いか電槽の金属薄板の厚みが薄い場合には、封着部に生じる残留応力が小さくなるため、割れは発生しないと考えら

40

50

* 【0043】[実施例2] 正極電槽4、負極電槽5およびシールフレーム11をステンレス304で作製したこと以外は実施例1と同様にしてカード型リチウム電池を組み立てた。

【0044】[比較例1] 実施例1と同様にして作製した極群を電槽であるコバールとこのコバールに対して接着性を有する環状に成形されたポリオレフィン樹脂によって囲まれた空間に収納し、140°Cの熱板で加圧しながら加熱して電槽を封着してカード型リチウム電池を作製した。

【0045】[比較例2] 正極電槽に極群収納部を凹状に加工していないコバール製金属薄板を用いたこと以外は実施例1と同様にしてカード型リチウム電池を組み立てた。

【0046】上記実施例1、2および比較例1、2で作製した電池を用いて耐熱性を評価する目的で高温放置による容量劣化を評価した。評価は、各電池を5個用意し、まず室温で10時間率の電流値で2.9Vまで満充電した後、100、125、150、175、200°Cの恒温槽内に100時間放置し、槽外に取り出して電池の温度が室温になったことを確認した後、充電と同じ10時間率の電流値で1.5Vまで定電流放電して放電容量を求め、先の充電容量に対する充放電効率を求める方法を行った。その結果は、表1に示すとおりである。

【0047】

【表1】

れる。

【0049】したがって、絶縁性セラミックスを介してピンホールのない金属薄板製から成る電槽を溶接することで水分の侵入を防止し、全固体リチウム電池本来の広い動作温度範囲と高い安全性を実現できるものである。なお、実施例ではコバール、ステンレス以外の金属、およびLiMn₂O₄、Li_{1-x}Ti_xO₂以外の活物質の実施例は記載しなかつたが、いずれも既存の材料であり、同じ効果が得られることは明白である。

【0050】

【発明の効果】以上のように、本発明に係るリチウム電池では、正極層と負極層とを活物質と無機固体電解質で形成し、電解質層を無機固体電解質で形成し、正極電槽と負極電槽を金属製薄板で形成すると共に、この正極電

槽と負極電槽との周縁部を表面に金属化部を設けた絶縁性セラミックスを介して封止したことから、電槽の封止部の耐熱性が向上し、全固体リチウム電池本来の広い動作温度範囲と高い安全性を実現できる。

【図面の簡単な説明】

【図1】本発明に係るリチウム電池の断面図である。

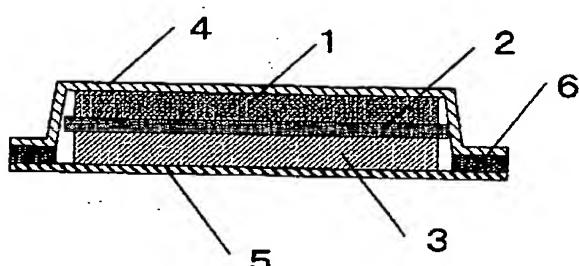
【図2】本発明に係るリチウム電池の封止部の拡大断面*

*図である。

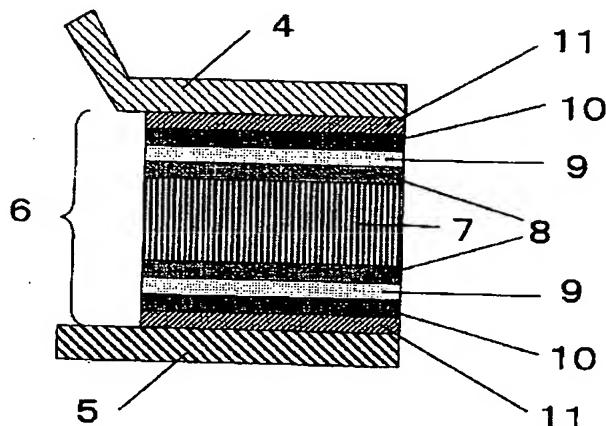
【符号の説明】

1…正極層、2…電解質層、3…負極層、4…正極電槽、5…負極電槽、6…低融点ガラス、7…絶縁性セラミックス、8…金属化部、9…ニッケルメッキ層、10…銀ろう層、11…シールフレーム

【図1】



【図2】



フロントページの続き

(72)発明者 北原 輝之
京都府相楽郡精華町光台3丁目5番地 京
セラ株式会社中央研究所内

(72)発明者 原 亨
京都府相楽郡精華町光台3丁目5番地 京
セラ株式会社中央研究所内

(72)発明者 大崎 誠
京都府相楽郡精華町光台3丁目5番地 京
セラ株式会社中央研究所内

(72)発明者 樋口 永
京都府相楽郡精華町光台3丁目5番地 京
セラ株式会社中央研究所内

F ターム(参考) 5H024 AA02 AA03 BB14 CC04 CC06
DD01 DD02 DD03 EE01
5H029 AJ12 AK02 AK03 AL02 AL03
AM12 BJ04 CJ05 DJ02 DJ03
EJ01 EJ08